



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6: C04B 20/00, E21B 33/13		A1	(11) International Publication Number: <b>WO 97/28097</b> (43) International Publication Date: 7 August 1997 (07.08.97)
(21) International Application Number: PCT/EP97/00397		(74) Agent: MENES, Catherine; Etudes & Productions Schlumberger, Division Dowell, 26, rue de la Cavée, Boîte postale 202, F-92142 Clamart Cedex (FR).	
(22) International Filing Date: 29 January 1997 (29.01.97)		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TI, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TI, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(30) Priority Data: 9601176 31 January 1996 (31.01.96) FR		Published With international search report.	
(71) Applicant (for all designated States except CA FR US): SOFITECH N.V. [BE/BE]; Rue de Stalle 142, B-1180 Brussels (BE).			
(71) Applicant (for CA only): SCHLUMBERGER CANADA LIMITED [CA/CA]; 24th floor, Monenco Place, 801 6th Avenue, S.W., Calgary, Alberta T2P 3W2 (CA).			
(71) Applicant (for FR only): COMPAGNIE DES SERVICES DOWELL SCHLUMBERGER S.A. [FR/FR]; 50, avenue Jean-Jaurès, Boîte postale 360, F-92541 Montrouge (FR).			
(72) Inventors; and			
(73) Inventors/Applicants (for US only): BARET, Jean-François [FR/FR]; 108, boulevard Montparnasse, F-75015 Paris (FR).			
MAROY, Pierre [FR/FR]; 2, allée Charles-Nicolle, F-78530 Buc (FR).			

(54) Title: CEMENT ADDITIVES AND CEMENT COMPOSITIONS INCLUDING SAID ADDITIVES

## (57) Abstract

According to the present invention, it is proposed to use 50 micron screened solid particles as fluid loss control agents in cement compositions used for cementing oil, gas, water, and geothermal wells. The present invention relates also to cement compositions comprising 50 micron screened solid particles.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SG	Singapore
CG	Congo	KZ	Kazakhstan	SI	Slovenia
CH	Switzerland	LJ	Liechtenstein	SK	Slovakia
CI	Côte d'Ivoire	LK	Sri Lanka	SN	Senegal
CM	Cameroon	LR	Liberia	SZ	Swaziland
CN	China	LT	Lithuania	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
CZ	Czech Republic	LV	Latvia	TJ	Tajikistan
DK	Germany	MC	Moscow	TT	Trinidad and Tobago
DK	Denmark	MD	Republic of Moldova	UA	Ukraine
EE	Estonia	MG	Madagascar	UG	Uganda
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France	MR	Mauritania	VN	Viet Nam

5

**CEMENT ADDITIVES AND CEMENT COMPOSITIONS**  
**INCLUDING SAID ADDITIVES**

10 The present invention relates to additives for controlling fluid loss and intended more particularly for fluids such as oil industry fluids used in drilling, cementing, or stimulation operations in oil, gas, water, or geothermal wells and the like, or fluids used in civil engineering, such as the fluids included in the composition of certain concretes, for example, in particular those used for injection purposes or more generally in pumping operations. The invention also relates to fluids including the said additive.

15 It is known that slurries containing a hydraulic cement lose a fraction of their water when they come into contact with permeable materials, and in particular underground formations that are clayey or of any other type of rock that is permeable to a greater or lesser extent. This "fluid loss" phenomenon has effects that are negative both on the rheological properties of the slurry, reducing its fluidity, and thus making it more difficult to pump and possibly leading to stoppage, and on gas migration given that a slurry which is sensitive to 20 fluid loss is generally unlikely to oppose gas migration while the cement is setting, which can give rise to severe safety problems for operations performed on oil wells.

Also, fluid losses are generally not uniform; for example, they may be greater in hotter locations close to the bottom of the well or at the end of cementing. This is very harmful to the quality of operations performed.

25 Far from being strictly specific to cementing slurries for oil wells and the like, the problem of fluid loss is also encountered with concretes or other similar substances used in civil engineering and, for example, pumped for the purpose of being injected in shattering, e.g. in order to make the piles of a structure.

Such fluid loss is controlled by adding a fluid loss control additive to the cement slurry. 30 Such additives come in two broad classes: water-soluble polymers; and materials comprising finely-divided particles.

35 The water-soluble polymers most worthy of mention are substances derived from cellulose, such as hydroxyethyl cellulose and carboxymethyl cellulose, in particular, and synthetic polymers such as derivatives of acrylamide or alkylene-amine copolymers, or polyvinyl alcohol, in particular. In general, the mechanism implemented by water-soluble polymers relies on an increase in the viscosity of the aqueous phase of the cement slurry and a decrease in the permeability of the filter cake, i.e. the solid particles deposited on the walls

5 of the well by the cement slurry. Although in very widespread use, water-soluble particles nevertheless suffer from various limitations: if the aqueous phase is too viscous, then mixing with cement becomes very difficult. Also, such substances usually have a delaying effect on the setting of the cement. Finally, and this is not the least of the drawbacks, substances of synthetic origin are relatively expensive and can represent as much as half the  
10 cost price of a cement composition.

It is known that certain solid materials in the form of small particles have an effect on controlling fluid loss even if such materials are not usually added to a cementing composition for this purpose. This applies to clayey minerals such as bentonite which is commonly used for lightening cement slurries.

15 Finally, there exists a somewhat hybrid class of filter loss control agent constituted by materials of submicron size in suspension in a liquid, e.g. latex type polymer emulsions, in particular polyvinyl acetates, styrene-butadiene latices, and colloidal materials. Latices are synthetic materials comprising some of the most sophisticated and expensive of all additives used in this industry and as a result they are reserved for the most difficult  
20 applications, in particular preventing gas migrating through cement while the cement is setting.

The fluid loss controlling effect obtained with such solid materials is generally attributed to the pores between the grains of cement becoming plugged. However it must be recognised that the mechanism is far from being completely elucidated and probably implies various  
25 interactions between the solid particles themselves and the grains of cement. Attapulgite, a material which is used as a substitute for bentonite in environments that are very salty thus has no recognized fluid loss controlling effect. Also, the performance of materials of mineral origin are well below the performance of water-soluble polymers.

30 There thus remains a presently unsatisfied need for fluid loss control agents that are easily available, that provide good performance, and that are compatible with most of the densities commonly used for cementing slurries (10 ppg to 25 ppg, i.e.  $1.2 \text{ g/cm}^3$  to  $3 \text{ g/cm}^3$ ).

35 The present invention proposes using an additive as a fluid loss control agent in a cementing slurry, which additive is constituted by solid particles passed through a 50 micron or smaller screen, e.g. a 20 micron screen or a 10 micron screen. The screening preferably serves to eliminate all particles having a diameter greater than 10 microns.

36 The concept of screening, also known as riddling, as used in the definition of the invention refers to a mechanical separation operation excluding, for example, the use of electrostatic precipitators filters for separating small particles, and excluding liquid-based methods.

5 More generally, the term must be understood as covering any means of classifying fine particles using a dry process, in particular by means of cyclones or by rotation, vibration, or any other equivalent means. By eliminating larger-sized particles in this way, a much narrower grain size curve is obtained characterised by quite a sharp break at the large-sized particle end, it nevertheless being emphasised that the mean size of the screened particles is  
10 much smaller than the screen mesh size. Thus, 50 micron screening serves, in fact, to eliminate the great majority of particles with a size greater than 20 microns.

Solid particles suitable for use after screening in accordance with the invention are preferably particles of mineral origin. Particularly preferred are substances based on silica, such as silica flour for example which is generally obtained by grinding fine sand, or fly  
15 ash, a residue from burning coal. In general, it is preferable to use substances in which the particles are more or less spherical.

Silica flour and fly ash are two additives that are very commonly used in cement compositions, in particular for the purpose of lightening a slurry. Fly ash has the advantage of having a pozzolanic character, i.e. in the presence of water it reacts with the calcium hydroxide of Portland cement to form compounds possessing the properties of a cement.  
20 Being of smaller density than Portland cement and of similar grain size, such substances thus replace the Portland cement in full or in part.

If particles of larger size are not eliminated, then silica flour and fly ash do not have any significant effect on controlling fluid loss. In contrast, merely by being screened, these  
25 substances become good fluid loss control agents.

Results are further improved with improved dispersion of the solid particles. A dispersing agent is therefore preferably added to cement compositions of the invention. In this context, it is possible in particular to use the dispersants commonly employed for preparing cement slurries, and also known as superplasticizers. By way of example, mention can be  
30 made of sulfonates such as polymelamine sulfonate (PMS), polynaphthalene sulfonate (PNS), lignosulfates, polystyrene sulfonates, hydroxylated polysaccharides, and certain hydroxycarboxylic acids.

The invention also provides a cementing slurry comprising a hydraulic cement, in particular of the Portland type, a fluid loss control agent of the invention, a dispersing agent, and an aqueous phase. In known manner, the following can be added to this basic slurry: a cement  
35 setting retarder, or on the contrary an accelerator, a weighting agent, and other additives known in this art.

5 Concentrations of 2% to 5% (weight concentrations relative to the weight of cement) suffice to obtain a large reduction in fluid loss. Best results are usually obtained with concentrations of about 15%, and more generally with concentrations lying in the range 10% to 20%.

10 With compositions that are very well dispersed, the fluid loss control agent can be at a slightly lower concentration.

15 Using the filter loss control agent of the invention, which is no more than a solid mineral additive, it is already possible to obtain fluid losses of less than 100 ml. If even lower values are desired, a higher performance fluid loss control agent, in particular a water-soluble polymer, may be added to the composition, but in much smaller quantity than would be required in the absence of the loss control agent of the invention.

Other details and characteristics of the invention appear from the following description of tests performed on various example compositions including the additive, and made with reference to the accompanying drawings, in which:

- Figures 1 and 1-bis are grain size curves for fly ash, before and after 50 micron riddling, and also, by way of comparison, for various Portland cements used for cementing wells;
- Figure 2 shows grain size curves for silica flour, before and after 50 micron riddling;
- Figure 3 is a bar chart showing fluid losses at 85°C as a function of various quantities of screened or unscreened fly ash added to the composition, the percentages being given relative to the weight of cement;
- Figure 4 is a bar chart showing fluid losses at 85°C as a function of various quantities of riddled or unriddled silica flour added to the composition, the percentages being given relative to the weight of cement;
- Figure 5 applies to a 1.44 g/cm<sup>3</sup> (i.e. 12 ppg) cement slurry and shows the effect on fluid loss of increasing the concentration of dispersing agent, for various different concentrations of 50 micron screened fly ash; and
- Figure 6 applies to a 2.04 g/cm<sup>3</sup> (i.e. 17 ppg) cement slurry and shows the effect on fluid loss of increasing the concentration of 50 micron screened fly ash.

35 To illustrate the invention in non-limiting manner, tests have been performed on two types of material: fly ash (Examples 1, 3, and 4), and silica flour (Example 2).

## 5 Example 1

Fly ash is a residue produced by burning coal, in particular in coal-burning electricity power stations. In modern installations, the burners are fed with coal that has been pulverised. The unburned fraction is vaporised in flue gas and after cooling it condenses in the form of finely-divided particles that are approximately spherical. Electrostatic precipitators in the chimneys capture all particles smaller than 200  $\mu$ .

10 The major component of fly ash is a glass composed mainly of silica, alumina, and iron oxides. These oxides which preferably constitute more than 70% of the composition are accompanied by lime, alkali compounds, magnesium compounds, and a small amount of unburned fuel matter. In practice, the composition of ash varies considerably as a function

15 of the origin of the coal, the type of burner, and various other factors. The volatile compound fraction (water and carbonates) is generally in the range 8% to 12%. The density of fly ash lies in the range 2 g/cm<sup>3</sup> to 2.7 g/cm<sup>3</sup>.

For the tests described herein, the fly ash used was class F in the ASTM classification. As can be seen by comparing Figures 1 and 1-bis, prior to riddling (Figure 1, solid line curve),

20 the grain size distribution of such fly ash is practically identical to the distribution of class G Portland cement of the kind commonly used for cementing oil wells. The grain size curves marked in Figure 1-bis correspond to oil industry cements sold under the following names: Cemoil-1 (curve C1), Dyck G Gulf-3 (curve C2), and Black Dyckerhoff-4 (curve C3).

25 After passing through the 50 micron riddle, the majority of the particles had a diameter lying in the range 1 micron to 10 microns (Figure 1, dashed line curve).

The fluid losses of cements prepared using screened and unscreened fly ash were measured in compliance with API (American Petroleum) standards on the basis of elementary cementing intended solely for testing feasibility, and constituted by 600 ml of slurry made

30 up of:

- 1046 grams (g) of class G cement;
- 240 g of water;
- ash in the percentages given (relative to the weight of cement).

The histograms in Figure 3 (white bars corresponding to material screened in accordance with the invention, shaded bars corresponding to non-screened material) indicate clearly that non-screened fly ash as used in the prior art has no effect in controlling fluid loss regardless of the concentration of fly ash in the cement composition. In contrast, with only

5 5% of screened fly ash, fluid losses are already divided by four. Fluid loss control is further improved if the quantity of screened fly ash is increased, with best results appearing at concentrations of about 20%.

**Example 2**

10 In this example, silica flour was used instead of fly ash. The silica flour was obtained by grinding fine sand (Schlumberger Dowell reference D66 for the non-screened silica flour and C600 for the screened silica flour). The grain size distribution of the substance is shown in Figure 2 where the dashed line curve is before the classification operation and the solid line curve after. It may be observed that the distribution is very similar to that obtained using fly ash.

15 As in the preceding example, the solid particles were added to an elementary cementing base (fresh water + class G cement). It can be seen in Figure 4, in which the silica concentrations are percentages relative to the weight of cement, that the additive constituted by non-screened silica flour (shaded bars) has no effect in controlling fluid loss, whereas on the contrary a remarkable effect was obtained when using 50 micron riddled silica flour (white bars).

20 The looked-for effect was again obtained even at very low concentrations. The smallest fluid losses were obtained for compositions containing 20% of screened silica flour.

25 **Example 3**

After testing feasibility, attempts were made to prepare compositions that had been optimized by adding a dispersing agent. For these tests, a dispersing agent of the polynaphthalene sulfonate type (Schlumberger Dowell reference D80) was used.

30 Formulations having a density of 1.44 g/cm<sup>3</sup> were prepared by varying the concentration of the dispersing agent (concentrations given in gallons per 94 pound sack of cement; a concentration of 0.1 gal/sk or 0.1 gps thus corresponds to 0.90 litres of dispersing agent per 100 kg of cement), and by varying the concentration of screened fly ash, using the same fly ash as in Example 1 (the percentages given are weight percentages relative to the cement).

35 In application of the recommendations of the API standard, measurements were performed only when the test composition was indeed stable, i.e. when it did not present phase separation giving rise to free water and settling.

5 The values of fluid loss measured for the various formulations are plotted in Figure 5. It can again be seen that fluid loss control is improved with increasing concentration of screened fly ash. Also, adding a dispersing agent further significantly improves control, with an optimum at around 0.1 gal/sk. At greater concentrations, there is no further improvement in fluid loss control. Best results were obtained with 15% screened fly ash

10 and 0.1 gal/sk of dispersing agent.

#### Example 4

Tests were made to verify that cementing slurries of relatively high density (17 ppg or 2.04 g/cm<sup>3</sup>) could likewise be prepared using a fluid loss control agent of the invention. To do

15 this, various formulations were prepared, all including a dispersing agent (0.05 gal/sk) and a cement setting retarder (0.05 gal/sk).

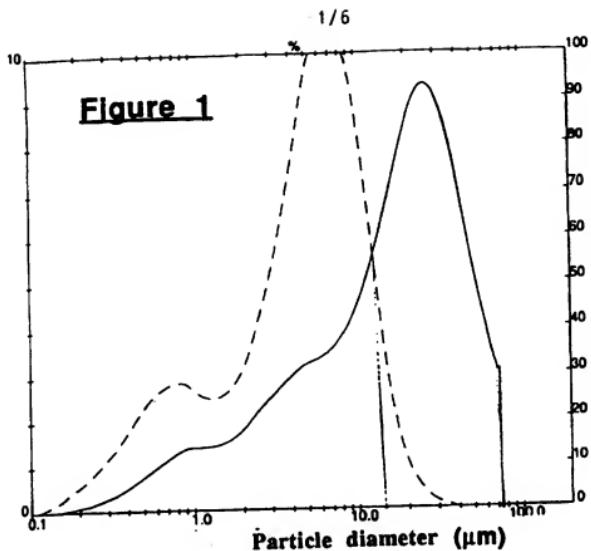
Figure 6 shows that fluid losses of about 100 ml could be obtained at 85°C for fly ash concentrations of about 25% to 30% (relative to the weight of cement) for the concentrations of retarding agent and dispersing agent used in these tests.

20 The remarkable performance obtained in this way merely by adding a mineral additive and before attempting any optimization of the properties of the slurry needs to be emphasized.

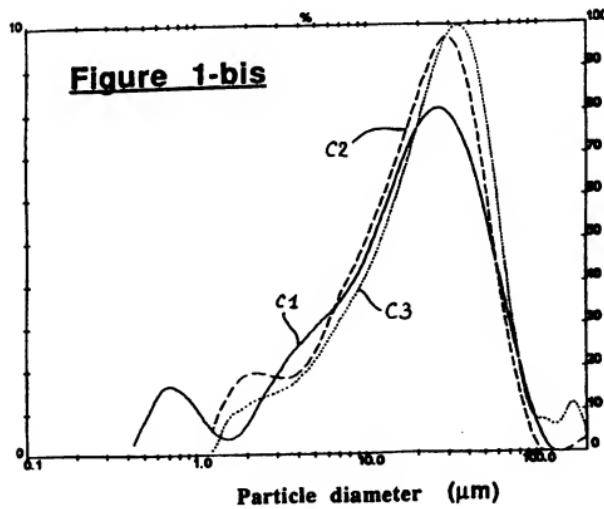
5

## CLAIMS

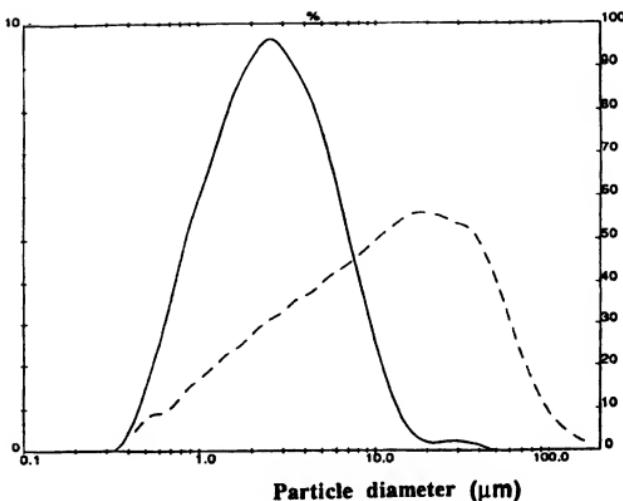
1. A fluid loss control agent for a slurry for cementing oil, gas, water, and geothermal wells and the like, characterised in that it is constituted by 50 micron screened solid particles.
- 10 2. A fluid loss control agent according to claim 1, characterised in that the solid particles are 20 micron screened.
3. A fluid loss control agent according to claim 1 or 2, characterised in that at least 90% of the screened particles are less than 10 microns in size.
- 15 4. A fluid loss control agent according to any preceding claim, characterised in that the screened solid particles come from fly ash.
5. A fluid loss control agent according to any one of claims 1 to 3, characterised in that the screened solid particles come from silica flour.
6. A cementing composition for cementing oil, gas, water, and geothermal wells, and the like, characterised in that it includes a fluid loss control agent according to any one of claims 1 to 5.
- 20 7. A cementing composition according to claim 6, characterised in that said fluid loss control agent is added at a concentration of 2% to 30% by weight (relative to the cement).
8. A cementing composition according to claim 7, characterised in that it comprises 10% to 20% by weight (relative to the cement) of a fluid loss control agent according to any one of claims 1 to 5.
- 25 9. A cementing composition according to any one of claims 6 to 8, characterised in that it further includes a dispersing agent.



**Figure 1-bis**

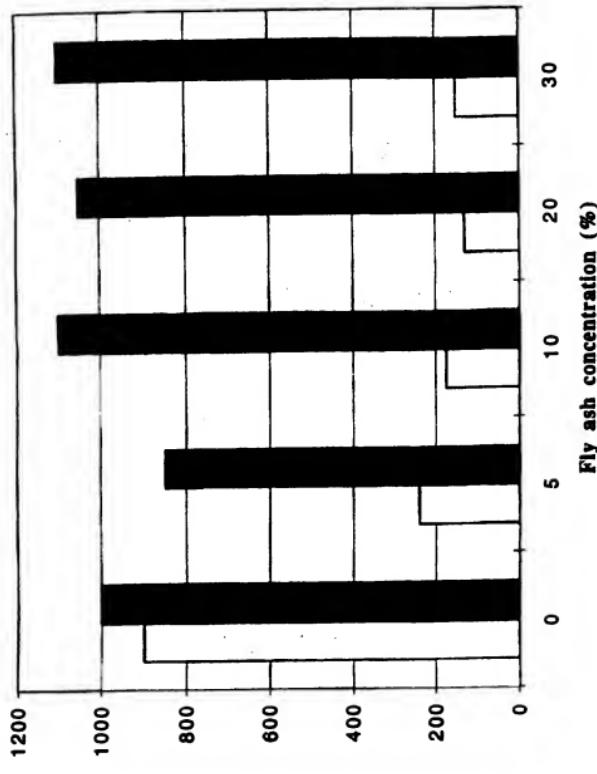


2 / 6



**Figure 2**

**Figure 3**



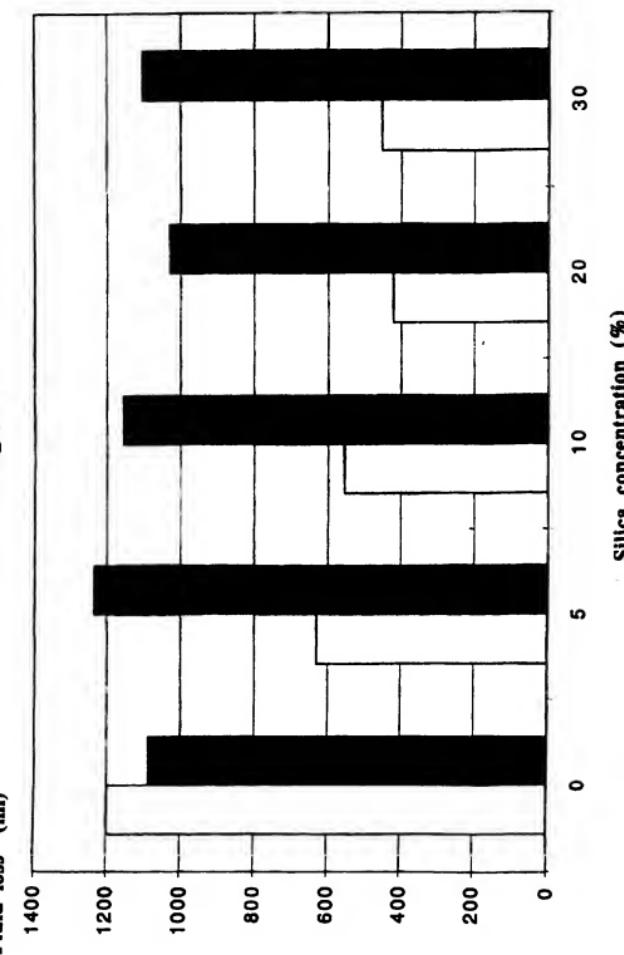
**Figure 4**

Figure 5

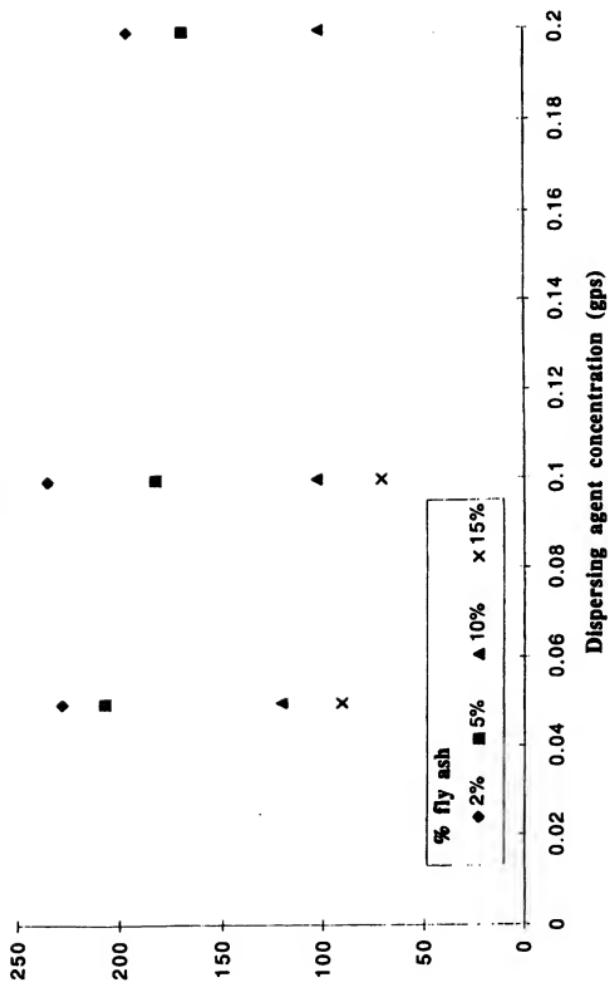
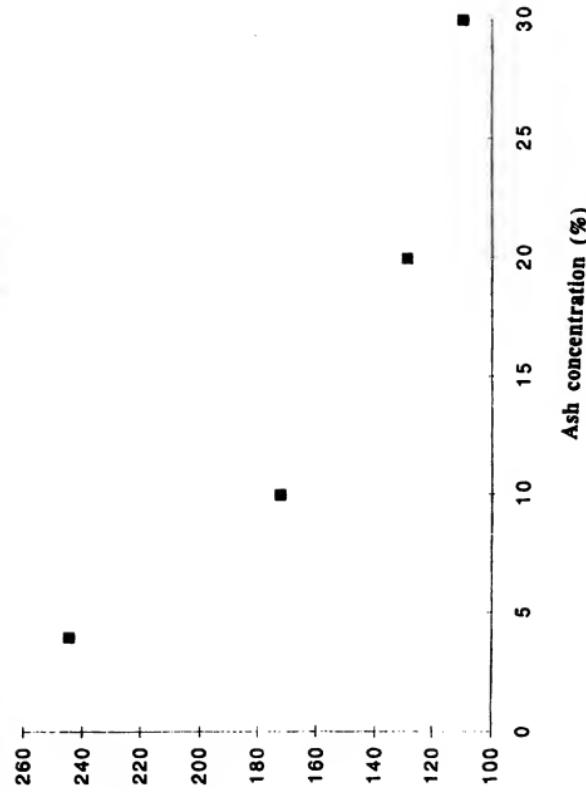


Figure 6



A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C04B/00 E21B33/13

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 C04B E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 212 489 A (ELKEM) 26 July 1989 see page 4, line 4 - line 12 see page 5, line 10 - line 32; claims 1-8 ---	1,4-7,9
X	GB 2 179 933 A (ELKEM) 18 March 1987 see page 2, line 48 - page 3, line 7; claims 1-5 ---	1-8
A	US 4 482 381 A (R.D.SPITZ) 13 November 1984 see column 2, line 3 - line 14 ---	1
A	US 5 229 019 A (G.T.FORREST) 20 July 1993 see claim 1 ---	1
A	US 4 941 536 A (L.E. BROTHERS) 17 July 1990 see column 5, line 31 - line 45 ---	1,4,5
	-/-	

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or otherwise assist in establishing the priority date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other cited documents, such combination being obvious to a person skilled in the art.

\*Z\* document member of the same patent family

1

Date of the actual completion of the international search  23 April 1997	Date of mailing of the international search report  29.04.97
Name and mailing address of the ISA European Patent Office, P.B. 5018 Patentdienst 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Authorized officer  LIBBERECHT, E

Intern. Application No.  
PCT/EP 97/08397

## C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 95 27685 A (N.V. KEMA) 19 October 1995 see claims 1-13 -----	1-4

## INTERNATIONAL SEARCH REPORT

Information on patent family members

Internal J Application No

PCT/EP 97/00397

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2212489 A	26-07-89	HK 7893 A US 4935060 A	12-02-93 19-06-98
GB 2179933 A	18-03-87	BR 8604196 A CA 1266557 A DE 3629769 A DK 158483 B FR 2587988 A NL 8602122 A, B, SU 1799369 A US 4933031 A	28-04-87 13-03-90 05-03-87 05-04-94 03-04-87 01-04-87 28-02-93 12-06-98
US 4482381 A	13-11-84	US 4569694 A	11-02-86
US 5229019 A	28-07-93	US 5229018 A US 5246602 A WO 9214032 A US 5102866 A	28-07-93 21-09-93 28-08-92 07-04-92
US 4941536 A	17-07-90	US 5049288 A	17-09-91
WO 9527685 A	19-10-95	NL 9400564 A CA 2186248 A EP 0758308 A	01-11-95 19-10-95 19-02-97

THIS PAGE BLANK (USPTO)